



Hydrothermal gasification of sewage sludge and model compounds for renewable hydrogen production: A review



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ABSTRACT

Sewage sludge is bio-solid with high moisture content generated from wastewater treatment plants. Due to the avoidance of energy-intensive dewatering, hydrothermal conversion of sewage sludge becomes a promising technology to simultaneously achieve energy recovery and solid waste management. In order to obtain an entire understanding of applicability of hydrothermal gasification for hydrogen rich gas production from sewage sludge, this review article discussed hydrothermal conversion and gasification processes in terms of fundamental principles, operating conditions, partial oxidative gasification, and detrimental effects of intermediates. Furthermore, since organic compounds in sewage sludge are mainly composed of carbohydrates, proteins, lipids, and lignin, this article comprehensively reviewed hydrogen production from these biomass model compounds and their hydrolysis products under sub- and supercritical water. Additionally, introduction of alkali salts and heterogeneous catalysts to enhance hydrogen yield under mild temperatures and pressures in hydrothermal gasification process was also discussed. Based on bench and pilot scale studies, supercritical water gasification of sewage sludge for hydrogen production is feasible in terms of technical and economic evaluation. Given issues concerning corrosion, plugging and high operating cost, a combined supercritical water gasification and catalytic hydrothermal gasification concept is proposed as a practical strategy to directly harness hydrogen from sewage sludge in future applications.

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1. Introduction

Sewage sludge is a semi-solid residue generated from wastewater treatment plants (WWTPs). Wastewater treatment system is generally integrated with a series of physical, chemical, and biological treatment units. After anaerobic digestion, the sludge is subjected to conventional mechanical dewatering which can reduce the moisture content to around 80 wt%. Sewage sludge is rich in organic matter and nutrients (such as nitrogen and phosphorus) and mainly composed of proteins (~40%), lipids (10–25%), carbohydrates (14%), lignin and ash (30–50%) [1,2]. Depending on the characteristics of wastewater sources and wastewater treatment process, heavy metals (i.e. Cd, Cr, Cu, Zn, Pb, Ni, and As), pathogens or other microbiological pollutants, persistent organic pollutants (POPs) (i.e. polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins, pesticides, nonyl phenol, and linear alkyl sulfonates, etc.) [3] can be entrained in sewage sludge, posing potential risks to environment and human health if it is not appropriately treated.

Due to urbanization and increasingly stringent regulations for the quality of discharged water, the sludge generation from WWTPs is soaring worldwide. At present, the annual production of dry sludge in European Union is more than 10.96 million tons [4] and sludge production in China is estimated to reach 6 million dry tons per year [5]. Moreover, the cost used for sludge treatment represents almost 50% of the total capital cost of wastewater treatment process [6]. Therefore, a wide variety of sludge treatment technologies have been implemented, including three main categories, landfill disposal, land application, and incineration.

Landfill disposal not only occupies plenty of land but also generates a large volume of landfill leachates and gases resulting from the high moisture and organic matter contents in sewage sludge. The landfill leachates and gases can incur pollutions to surrounding water, air, and soil. Sometimes, the landfill site may even collapse due to insufficient strength of sludge. Moreover, metabolites in the leachates can be more toxic than its precursors [7]. Composting is a prominent technology for land application. However, the odor control is problematic both in the processing stage and storage areas [6]. Oleszczuk [8] reported composting could significantly increase the toxicity of sewage sludge, which may be associated with the increased mobility and bioavailability of metabolites [7]. On the other hand, the market for composted sludge is a prerequisite. Thus, suitable revenue for the composting facilities is required and more outlets for the final compost should be developed [6]. Given migrations of heavy metals and organic

pollutants, it may not be advisable to use sewage sludge derived compost for land application. Furthermore, due to the high calorific value in sludge (i.e. higher heating values for dry sewage sludge before and after digestion around 23 MJ/kg and 8.5–17 MJ/kg, respectively), energy recovery from sludge has attracted great attention recently [9]. The potential energy in sludge could be recovered using either biological or thermochemical processes. In particular, incineration can dramatically reduce the sludge volume. Nonetheless, before being fed into incinerator, the moisture content of sludge should be lowered down to 35% during pre-drying step, leading to high energy consumption [7]. To eliminate the energy-intensive drying process, hydrothermal conversion technology was introduced to recover energy from wet biomass waste.

Hydrothermal conversion is a thermochemical process to reform biomass in hot compressed water. Under elevated temperature and pressure, specifically when exceeding the critical point (374.3 °C and 22.1 MPa) of water, the density, static dielectric constant and ion dissociation constant of water drop drastically, which can accelerate the reaction rate substantially [10]. Due to those superior properties of hot pressurized water, it acts as a non-polar solvent and benign reactant with high diffusivity, excellent transport properties and solubility. Consequently, hydrothermal conversion technology has been widely applied for fuels and chemicals recovery from wet biomass and organic waste with high moisture content in the last two decades. As shown in Fig. 1a, hydrothermal conversion can be divided into (1) hydrothermal carbonization (180–250 °C) for hydrochar production [11,12], (2) hydrothermal liquefaction (about 200–370 °C, with pressures between 4 and 20 MPa) for heavy oil production and (3) hydrothermal gasification (near-critical temperatures up to about 500 °C) [13] to generate hydrogen rich gas under various conditions. From the perspectives of fossil energy shortage and environmental impacts, renewable hydrogen recovery from readily available wet biomass using hydrothermal gasification is desired in the long run. Kruse [14] summarized previous research work relating to supercritical water gasification (SCWG) of biomass without heterogeneous catalysts whereas Elliott [15], Guo et al. [16] and Azadi et al. [17] reviewed catalytic sub- and supercritical water gasification of biomass for hydrogen production. In recent years, more efforts have been made to explore strategies to enhance hydrogen yield and carbon gasification efficiency during hydrothermal conversion of biomass or wastes. Up-to-date information and comprehensive summary are imperative to highlight technical and economic feasibility of hydrothermal gasification technology for wet biomass waste management system, especially

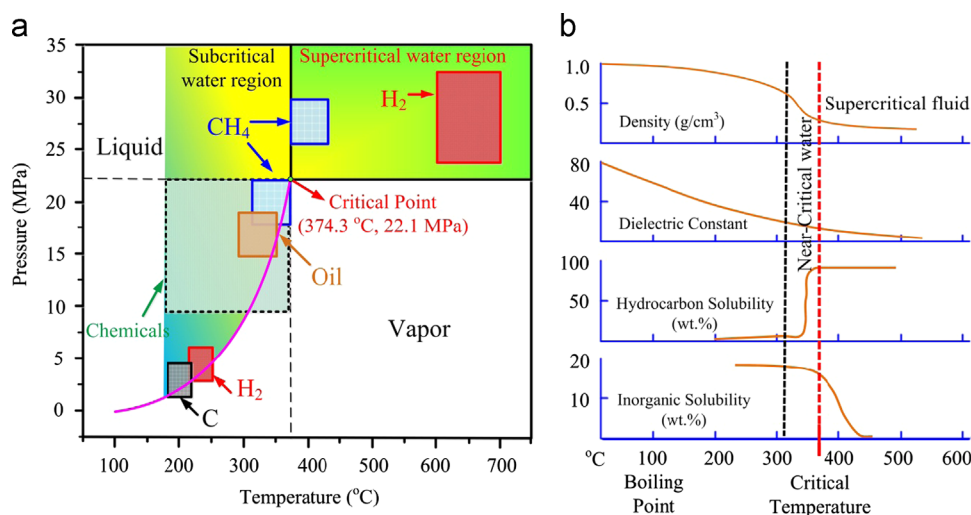


Fig. 1. Hydrothermal conversion options (a) and physical properties of water in subcritical, near-critical, and supercritical conditions at 25.3 MPa (b) (adapted from [13,14,18]).

Table 1

Some major advantages and assessment criteria of SCWG for hydrogen production.

Advantages [26–28]	Assessment criteria [29]
Energy-intensive prior drying is not required	Gas yield (i.e. total gas yield, H ₂ yield, CH ₄ yield)
Pressurized H ₂ rich fuel gas is more convenient for further applications	Molar fraction of product gas
Rapid and effective conversion reduced tar can be achieved	Gasification efficiency (GE)
Gas cleaning process is avoided and heteroatoms (N, S, and halogens) containing substances in the liquid phase are left in liquid phase	Carbon gasification efficiency (CGE)
Compact SCWG batch or continuous reactor can save space	Hydrogen gasification efficiency (HGE)
Inorganic elements in feedstocks in solid residues or liquid phase can be further recovered	Potential hydrogen yield (PHY)

sewage sludge, algae, and food wastes. This review covers three main parts: (1) effects of operating conditions, oxidants and intermediates on the hydrothermal gasification efficiency; (2) hydrothermal conversion and gasification of biomass model compounds and sewage sludge for hydrogen production; and (3) updates of catalytic hydrothermal gasification. Based on abovementioned aspects, perspectives relating to hydrothermal gasification of sewage sludge are presented.

2. Hydrothermal gasification technology

During conventional steam reforming of biomass to produce desired light gases, tar and char as well as higher hydrocarbons are greatly formed [19]. In 1985, Modell [20] initiated the SCWG process of maple wood sawdust without char formation. The mechanism of SCWG of biomass was described as a process involving hydrolysis of biomass in supercritical water (SCW) followed by further gasification of the produced aqueous oligomers [21,22]. Since SCWG of biomass is regarded as a high-pressure steam reforming, pre-drying could be avoided. Due to high solubility of water under SCW conditions, intermediates derived from biomass decomposition can be dissolved. As a consequence, remarkably reduced tar and coke formation can be expected in SCWG compared to classical gasification process [16,23]. Contrasting to the high temperature of conventional gasification (e.g. > 800 °C), SCWG of biomass materials is typically conducted at temperatures lower than 600 °C [24]. Table 1 summarizes the advantages and assessment criteria of SCWG. Though

SCWG of biomass is a complex process, the involved chemical reactions can be described by reactions (1)–(5) in Table 2 [25].

2.1. Role of water

Under normal temperature and pressure, water can exist in the form of ice, liquid, and vapor. When the temperature and pressure are elevated to above the critical point (374.3 °C and 22.1 MPa), water goes into supercritical state, where the gas and liquid phase become miscible (Fig. 1a) [30].

Fig. 1b illustrates the physical properties of water as the temperature increases under constant pressure 25.3 MPa. Water density decreases with the increase of temperature and a drastic decrease is observed at the critical temperature, resulting in broken hydrogen bonds in water. As a consequence, dielectric constant of water decreases from approximately 80 (at normal temperature and pressure) to 5 (at critical point) [16]. Dielectric constant is used to measure the polarity and solubility of the fluid. Lower dielectric constant reflects the high solubility of organic solvent and the low solubility of inorganic compounds [31]. Due to these unique properties, SCW has been regarded as an attractive reaction medium.

2.1.1. Acid/base catalysis and source of free-radicals

Below the critical point, ion product of water increases with elevated temperature by three orders of magnitude from $K_w = 10^{-14} \text{ mol}^2/\text{L}^2$ at 25 °C to $K_w \approx 10^{-11} \text{ mol}^2/\text{L}^2$ at 300 °C. Above this temperature, K_w decreases drastically to $10^{-20} \text{ mol}^2/\text{L}^2$ at 380 °C [32]. In subcritical water, ionic reactions are generally reinforced

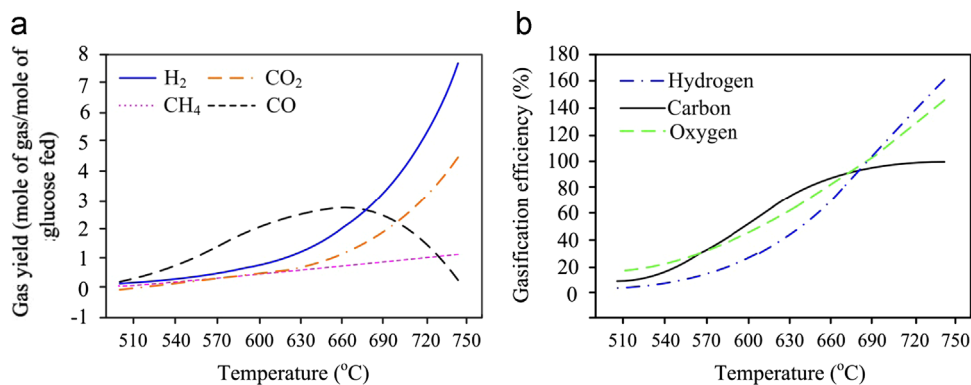


Fig. 2. Effect of temperature on gas yield (a) and gasification efficiency (b) in SCWG of glucose at 28 MPa and a 30 s residence time (adapted from [41,42]).

because of the higher concentrations of H^+ and OH^- . Because of high water density in subcritical water, hydrolysis is more preferable. Thus, high molecular weight compounds can be hydrolyzed to smaller fragments and dissolved into water for further oxidation and gasification [33] as a result of the acid/base catalysis of subcritical water. Water in hydrothermal conditions not only acts as reaction medium and reactant, but also as acid/base catalysts. The chemistry of acid/base catalysis and oxidation reactions for selective conversion of biomass to value-added products under hydrothermal conditions is given in a detailed review by Jin and Enomoto [34]. Besides, water was regarded as a catalyst in SCW for hydrogen production from formic acid degradation via decarboxylation and dehydration in reactions (6) and (7) [35].

In contrast to hydrolysis, free-radical reactions are favorable in low water density so that free-radical reactions dominate under high temperatures. Free-radical mechanism is composed of generation of radicals and fast free-radical reactions [16]. Hydroxyl radical, known as the most effective oxidant, is of great importance in supercritical water oxidation (SCWO). Reactions (8)–(13) which can form OH radicals significantly contribute to overall kinetics. Because the formed H_2O_2 in reaction (13) can subsequently generate two OH radicals, the less reactive oxidant hydroperoxyl radical (HO_2) can effectively generate three OH radicals in the presence of water [10]. Moreover, the delocalization of π -electrons by substitution of hydroxyl groups makes benzene rings readily cleaved to form small molecular weight compounds. In addition, heteroatoms can be also removed from the precursors at the same time. Ogunsola et al. [36] reported H radicals donated by SCW reinforced the saturation of heterocyclic rings, which subsequently opened to form hydrocarbons, sulfides, and NH_3 . Thus rupture of $-C-S-$ and $-C-N-$ bonds in heterocyclic ring by SCW hydrolysis can eliminate more N and S than pyrolysis and common hydrolysis.

2.1.2. Reactant and source of hydrogen

Apart from the role of water in acid/base catalysis, hydrolysis, and free-radical reactions, water also plays a critical role in hydrogen production as a catalyst and reactant. Park et al. [37] investigated SCWG of organic compounds in D_2O using RuO_2 as the catalyst. The CD_4 and D_2 in the gas products indicated all the H atoms originated from water. Kruse [14] summarized the hydrogen and methane formation from glucose in reactions (14) and (15). It can be deduced from the equations that H_2 formation is water dependent while CH_4 formation is water independent. Actually, Kruse et al. [23] reported that the hydrogen originating from water in SCWG could be as high as 50%.

2.2. Effect of temperature, pressure, and residence time

Both of ionic and free-radical reactions occur in hydrothermal environment but they are dependent on the properties of water

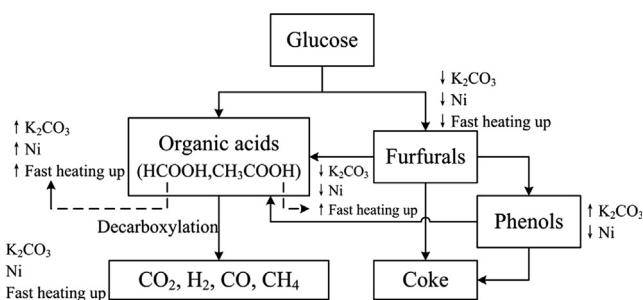


Fig. 3. Effects of heating rate and catalysts on products distribution of supercritical water gasification of glucose (adapted from [35]).

under various temperatures and pressures. Due to the high ion product of water, ionic reactions dominate below critical point of water [38]. Above the critical point, free-radical reactions are favored with hydrogen as the typical product [39]. The reaction mechanism is shifted from ionic reactions in the subcritical water to the free-radical reactions in supercritical water region [40]. Since the free-radical reactions are not affected by the properties of water, such as dielectric constant and ion product, the Arrhenius behavior is expected. However, as a result of the change of dielectric constant or ion product, the ionic reaction deviated from Arrhenius behavior [39].

In reactions (14) and (15), hydrogen formation is endothermic while CH_4 formation is slightly exothermic. According to the Le Chatelier principle, hydrogen formation is more favorable at high temperatures while CH_4 formation is preferred at high pressures [14]. In SCWG of corn cob and sodium carboxymethylcellulose (CMC), influences of experimental parameters on hydrogen yield exhibited the order of temperature > pressure > feedstock concentration > residence time [29]. As the residence time increased, hydrogen yield and CGE increased while CO yield decreased. Longer residence time can realize complete gasification of biomass which is expected within seconds when temperature is above 600 °C [7].

In Fig. 2, the yields of hydrogen and CO_2 increased with elevated temperature ranging from 480 to 750 °C under 28 MPa, especially above 660 °C [41]. However, the yield of CO gradually built up to a maximum value at 660 °C and decreased afterwards, which was supposed to be associated with the consumption of CO in water–gas shift reaction. Subsequently, Güngören Madenoğlu et al. [38] investigated simultaneous effects of temperature and pressure on hydrothermal gasification of glucose under 400–600 °C and 20–42.5 MPa within one hour. They found that CGE increased with the increasing temperature and decreased with increasing pressure. Compared to the effect of pressure, temperature plays a more important role in gas composition, which could be explained by the drastic decrease of dielectric constant of water

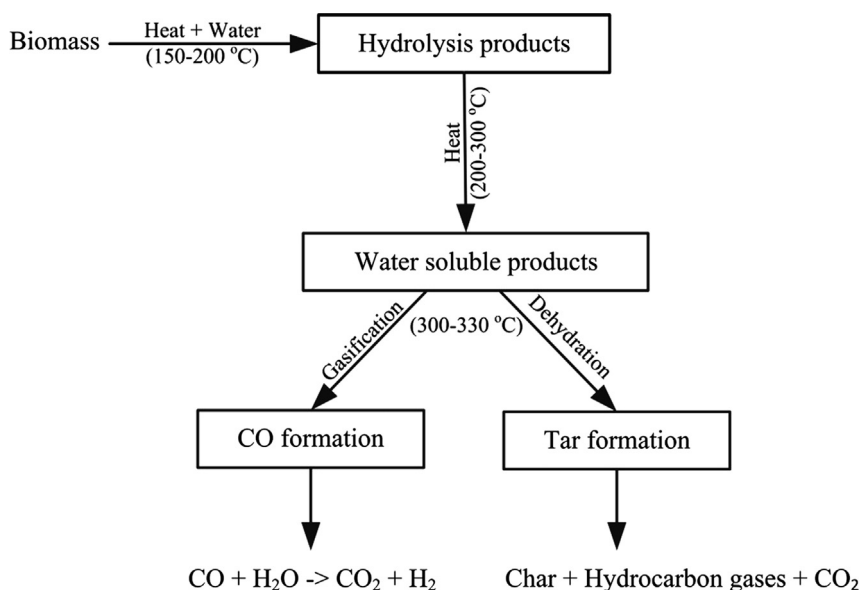


Fig. 4. Mechanistic scheme of hydrothermal gasification process (adapted from [46]).

at higher temperatures but only a slight increase of that with increased pressure. Decreased yields of H_2 as well as CO_2 and increased yield of CH_4 with increasing pressure under a constant temperature were attributed to methanation reaction. Overall, yields of H_2 , CH_4 , and CO_2 increased at higher temperatures.

In the catalytic hydrothermal gasification of glucose at 500 °C and 30 MPa, where glucose was used as model compound for cellulosic biomass, Sinağ et al. [35] demonstrated that the heating rate has a considerable influence on intermediates and products (Fig. 3). As the heating rate increased, yields of gas and formic acid increased while the yield of furfural decreased. Based on the assumption that formic acid was an intermediate of water–gas shift, higher gas yield may be associated with high yield of formic acid which suggested a higher water–gas shift activity. Furfural was suggested to be formed under subcritical conditions and may polymerize to form tar which was regarded as undesirable by-product. Therefore, slow heating rate decreased hydrogen yield due to the formation of coke/char [40].

2.3. Effect of oxidants on partial oxidative gasification

The addition of oxidants can improve the CGE. However, hydrogen yield cannot be constantly enhanced without limitation. Lu et al. [29] reported the hydrogen yield during gasification of corn cob and CMC decreased with the addition of $KMnO_4$ while that in glucose gasification increased initially and then decreased with the increase of H_2O_2 concentrations.

Due to competing pathways between gasification and oxidation reactions, oxidant concentration is an important parameter to optimize hydrogen production in SCWG [43]. Hydrogen yield was enhanced in partial oxidative SCWG of n-hexadecane by introduction of O_2 with O/C of 1.0 whereas the H_2/CO_2 ratio was decreased which may result from H_2 combustion with excess O_2 [44]. It is worth noting that SCWG reaction is an endothermic reaction while oxidation is an exothermic process. Guo et al. [43] reported that a small amount of oxidant accelerated hydrogen production but excess oxidant may result in combustion of H_2 and CO. Therefore, an appropriate amount of oxidants should be determined to improve gasification efficiency and hydrogen yield in SCWG of specific feedstock.

2.4. Effect of by-products/intermediates

Though tar and coke are reduced in SCWG compared to conventional pyrolysis, coke formation is commonly observed, especially during the heating up, causing reduction of CGE [45].

Onwudili and Williams [46] presented the simplified mechanistic scheme of hydrothermal gasification of biomass in Fig. 4 and pointed out that the conversion of hydrolysis products is critical during hydrothermal gasification. Because of the competition between dehydration route and gasification route, tar and char can be formed when water soluble products were dehydrated rather than retaining the hydrolysis products and converting them to hydrogen through gasification.

Therefore, tar and coke formation has been investigated during the degradation of glucose, cellulose, and other carbohydrates under hydrothermal conditions. 5-hydroxymethylfurfural (5-HMF) was confirmed to be an intermediate for the coke formation in SCWG of glucose under 300–400 °C and 25 MPa [47]. Müller and Vogel [45] examined tar and coke formation in hydrothermal processing of glycerol in a temperature range of 300–430 °C at 30 MPa. They found that coke was formed in subcritical temperatures (especially under 350–370 °C) with longer residence time while phenols and hydroquinone can be ruled out as the precursors of coke formation.

Acetic acid was the most refractory intermediate in SCW, which was reported to be stable above 600 °C [48]. During SCWG of glucose above 740 °C, only acetic acid in liquid effluents was detected whereas 42 compounds were found at 600 °C in the absence of catalysts. Phenol can also be very stable in SCWG. Guo et al. [49] reported SCWG of methanol was significantly retarded by acetic acid and phenol. Although acetic acid inhibited HGE, decarboxylation of HAc to CH_4 and CO_2 resulted in a great increase of CGE.

3. Hydrothermal conversion and gasification of biomass model compounds

3.1. Hydrogen production

Hydrogen is widely used in ammonia and methanol syntheses, fuel cells, hydrotreating and hydrogenation processes [24]. Due to lower cost of fossil fuels, coal gasification is currently the most

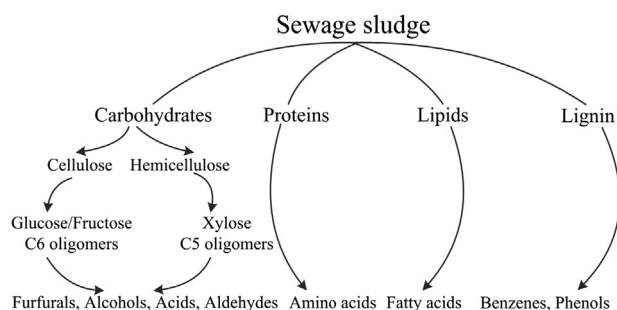


Fig. 5. Main organic components in sewage sludge and corresponding hydrolysis monomers under hydrothermal conditions.

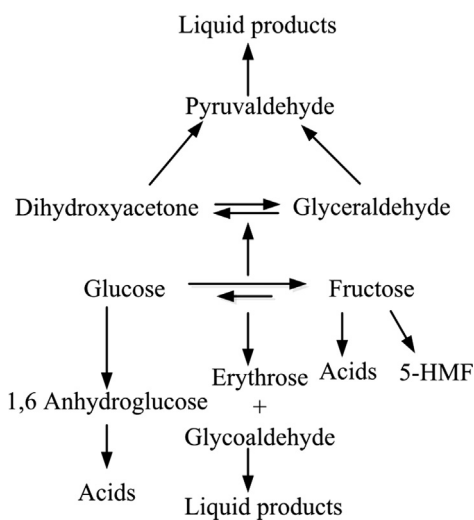


Fig. 6. Reaction pathways of glucose in sub- and supercritical water (adapted from [54]).

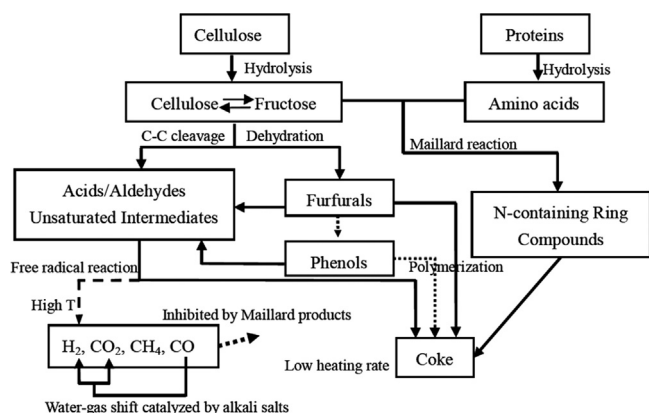


Fig. 7. Interactions of cellulose and proteins in hydrothermal gasification (adapted from [60]).

important industrial hydrogen production process. To lessen the dependence on fossil fuels, hydrothermal gasification of wet organic waste has been developed to generate hydrogen by maintaining water in the slurry feedstocks via exerting increased pressure. Aqueous phase reforming (APR) is a process typically conducted under 175–265 °C and 3.4–5.6 MPa [50]. Cortright et al. [51] demonstrated APR of oxygenated hydrocarbons (i.e. sugars and alcohols) to generate hydrogen rich fuel gas using platinum-based catalysts. Using a high throughput batch reactor, Huber et al. [52] discovered a non-precious metal catalyst, which was prepared by adding Sn to Raney-Ni catalysts, to significantly suppress the rate of methane formation while retaining the rate of

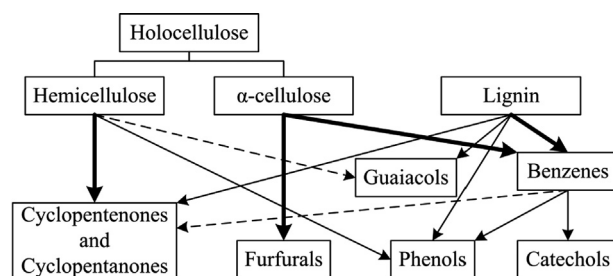


Fig. 8. Degradation pathways of lignin, holocellulose and cellulose in sub- and supercritical water (adapted from [63]).

hydrogen production. However, the hydrothermal stability of Raney-NiSn is a major concern when employed in SCW.

In order to make APR commercially viable, increased reaction rates are desired by increasing the temperature to near-critical or supercritical conditions. Meanwhile, as the objective of SCWG is hydrogen production, the increased temperature may also increase the undesired alkanes formation, thereby decreasing hydrogen yield [50]. Hence, effective catalysts for selective hydrogen production under SCWG of biomass are required. Hydrogen is generated from reforming reactions via C–C cleavage followed by water–gas shift while alkanes are mainly formed via C–O cleavage followed by hydrogenation. Effective catalysts should possess high activities in C–C cleavage and water–gas shift with suppressed C–O cleavage [53]. The catalytic hydrothermal gasification process for hydrogen production will be discussed in details in Section 4.

3.2. Hydrogen production from biomass model compounds

Recently, many researchers have used lignocellulosic biomass and biomass model compounds as feedstocks in hydrothermal gasification for hydrogen production. These studies provided fundamental information on application experience and mechanism of hydrothermal gasification process. However, the main organic compounds in sewage sludge are carbohydrates, proteins, lipids, and lignin, which can be decomposed to a mixture of furfurals, alcohols, carboxylic acids, aldehydes, amino acids, fatty acids, benzenes, and phenols under hydrothermal conditions (Fig. 5). It is necessary to understand hydrothermal decomposition and gasification of simple model compounds before discussing the feasibility and performance of hydrothermal gasification of sewage sludge for hydrogen production. Furthermore, control strategies to maximize hydrogen yield and selectivity may be applicable for sewage sludge.

3.3. Carbohydrates

Cellulose and hemicellulose are carbohydrates in biomass. Since products distribution from hydrothermal conversion of glucose are almost the same as that of cellulose, glucose is proved to be the primary hydrolysis product of cellulose [14]. Thus, glucose is widely used as a biomass model compound in SCWG. The decomposition pathways of glucose and fructose under 300–400 °C and 25–40 MPa with a residence time of 0.02–0.2 s are depicted in Fig. 6 [54]. The products from glucose decomposition were fructose (from isomerization), 1,6-anhydroglucose (from dehydration), erythrose and glyceraldehyde (from C–C bond cleavage). Reverse aldol condensation and double bond rule were responsible for the C–C bond cleavage. Knežević et al. [55,56] also conducted hydrothermal conversion of glucose under 300–350 °C with longer residence time ranging from 10 s to 10 d. Water production predominated in the first 5 min whereas gas and char were favored afterwards. Water and solvent soluble products

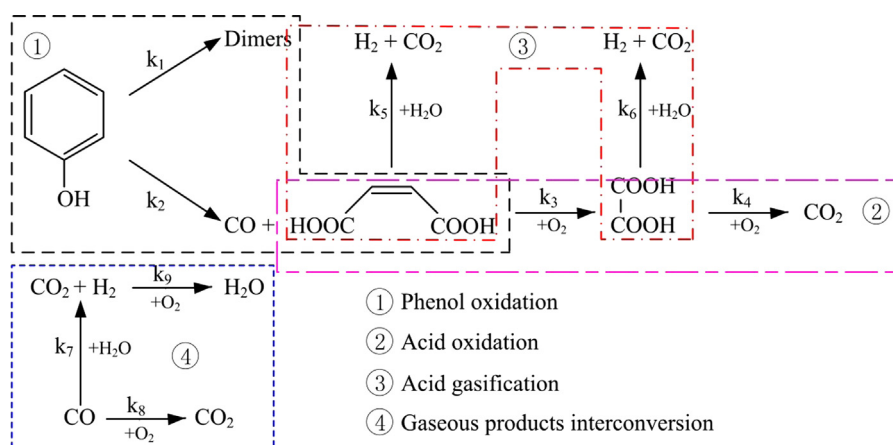


Fig. 9. The pathways of partial oxidation of phenol (adapted from [71]).

formed a polymerized oily component with lower oxygen content than glucose, leading to a 50% increase in energy density. The overall theoretical reaction for SCWG of glucose is summarized in reaction (16). Susanti et al. [48] investigated the non-catalytic SCWG of glucose at 600–767 °C with residence time of 15–60 s. The maximum hydrogen yield of 11.5 mol H₂/mol glucose could be achieved at 767 °C and 25 MPa with the glucose concentration of 1.8 wt%, which was quite close to the theoretical value of 12 mol H₂/mol glucose in reaction (16).

The rapid hydrolysis of cellulose to glucose and oligomers is the first reaction step of phyto biomass [57]. However, hydrolysis of cellulose is changed from heterogeneous on the cellulose crystal surface to homogeneous above the critical point of water [26]. The conversion rate of hydrolysis products under subcritical conditions was faster than hydrolysis of cellulose, while hydrolysis of cellulose under supercritical conditions was more than one order of magnitude faster than decomposition of hydrolysis products of cellulose. Thus, higher hydrolysis products yield was found in SCW than in subcritical water [58]. A simplified reaction scheme of cellulose is shown in Fig. 7. High ion product of water in subcritical water resulted in more furfural production and low gas yield. The furfural could be either dissolved or polymerized to form coke. On the other hand, gas yield increased under SCW because of the free-radical reactions. Based on non-catalytic gasification of cellulose in SCW [59], cellulose loading and water density are two effective variables controlling the gas product selectivity. At 500 °C and 0.08 g/m³ water density, CH₄/H₂ molar ratio decreased remarkably from 18.93 to 0.76 when the cellulose loading was increased from 5 to 33.3 wt%.

Hemicellulose is a copolymer composed of pentose, hexose, and uronic acid units [61]. Xylan is used as a model substance for hemicellulose in SCW. Similar to decompositions of glucose and fructose in SCW, retro-aldol condensation and dehydration contributed to the overall reaction rate [62]. Strategies for SCWG of cellulose can be applied for hemicellulose.

3.3.1. Lignin

Carrier et al. [63] reported that carbohydrates produced five carbon-containing compounds (cyclopentanones, furfurals and cyclopentenones), while six carbon-containing compounds (phenols, guaiacols, benzene) were derived from lignin under sub- and supercritical conditions (Fig. 8). High lignin content had an adverse effect [64] whereas high alkali salts had a positive effect [65] on the hydrogen yield in SCWG. The interactions between lignin and intermediates from cellulose/xylan decreased hydrogen yield via hydrogen donation. Moreover, cellulose generates higher

hydrogen during SCWG, while lignin is prone to produce more CH₄. CH₄ fraction was increased as the water density increased by manipulating the pressures during SCWG of alkylphenols (model compounds of lignin) catalyzed by Ru/γ-Al₂O₃ [66]. Resende et al. [59,67] investigated the non-catalytic SCWG of cellulose and lignin in quartz capillary reactors with a concentration of 9 wt% and 0.08 g/cm³ water density at 600 °C. Comparison of gas compositions in syngas from cellulose and lignin showed that CH₄/H₂ ratio increased with higher lignin loading but decreased with higher cellulose loading. Interestingly, CH₄ and CO₂ were the major products in non-catalytic SCWG of lignin. More CH₄ formation was probably related to the cleavage of methyl in lignin structure whereas less methyl substituents are contained in cellulose. The higher CO₂ yield in cellulose than lignin may be attributed to 49 wt% O in cellulose and only 27 wt% O in lignin.

3.3.2. Phenols

Phenols, which originate from lignin as well as carbohydrates in biomass, are rather inert in SCWG. As a result, the degradation of phenols becomes problematic for complete gasification of biomass and thus it has attracted extensive research attention [14]. A small amount of phenol can significantly diminish hydrogen yield and gasification efficiency of glucose even under 24 MPa and 400–550 °C [68]. Similar to proteins [28,60], this negative effect on SCWG may be attributed to the role of phenol as a free radical scavenger.

Higher dry matter loading can increase phenol yield and therefore hinder the complete SCWG of biomass [23]. By adding KOH, more than 99% gasification rate of pyrocatechol was obtained at 700 °C in 1 min [65]. In addition, introducing a small amount of oxidants in SCWG is another effective way to achieve nearly complete conversion. Xu et al. [69] reported a maximum hydrogen yield of 0.245 mol/mol phenol with molar ratio of 46.2% was obtained at 500 °C when an oxidation coefficient (oxidant added/oxidant needed for complete oxidation) of 0.6 within 3 min was employed in the presence of Na₂CO₃. Guan et al. [70,71] investigated the partial oxidative gasification of phenol in SCW and proposed the following reactions pathways (Fig. 9): (1) phenol oxidation, (2) acid oxidation, (3) acid gasification, and (4) gaseous products interconversion. Based on the abovementioned mechanism, the derived kinetic model fitted the experimental data very well in terms of predominant reactions and gaseous products distribution. Complete decomposition of phenol cannot be achieved but lower concentrations of oxygen could enhance the acid gasification and water–gas shift by inhibiting the oxidation process.

3.3.3. Proteins and amino acids

As proteins account for a large portion in sewage sludge, it is essential to understand the decomposition of proteins or amino acids in hydrothermal conditions. Subcritical water technology is considered as an effective method to extract amino acids from proteinaceous waste via the hydrolysis of proteins. Sato et al. [72] investigated the behavior of five selected amino acids (alanine, leucine, phenylalanine, serine, and aspartic acid) in hydrothermal conditions under 200–430 °C at 20 MPa. The overall decomposition of amino acids followed first order reaction. Two main reaction pathways of these amino acids were identified: (1) decarboxylation to produce carbonic acid and amines; and (2) deamination to produce ammonia and organic acids as in the case of aspartic acid. In addition, interconversion of amino acids from hydrolysis of proteins may take place. Under saturated subcritical water, the transformation and decomposition of amino acids may be easier due to the decreased overall stability in the mixed amino acids [73]. Klingler et al. [74] demonstrated model compounds of proteins (i.e. alanine and glycine) could be hydrothermally converted into value-added amines under 250–450 °C and 34 MPa with a residence time of 2.5–35 s.

Apart from subcritical water hydrolysis, SCWG of proteins or amino acids are widely explored. DiLeo et al. [75] claimed that glycine is more resistant than phenol in SCWG. After SCWG of glycine more than 1 h, glycine was significantly retained in the liquid phase. The CO was found to be the major product gas. Kruse et al. [28] found that SCWG of protein-containing biomass resulted in an unexpected low gas yield even under a high concentration of alkali salts. Subsequently, Kruse et al. [60] carried out a comparative hydrothermal gasification of model phyto mass (i.e. glucose+potassium salts) and model zoo mass (i.e. glucose+potassium salts+alanine) to investigate the influence of

proteins on product gas composition. It was reported that the addition of alanine into glucose/KHCO₃ decreased gas yield and increased the CO yield as well as dissolved organic carbon (DOC) in liquid solution. It is assumed that Maillard reaction occurred in the presence of proteins, which resulted from the interaction of degradation products of carbohydrates and proteins. The nitrogen containing compounds from interactions of amines and aldose sugars via Maillard reaction can further form free radical scavengers. The free radical scavenger is a stable free radical which is not reactive enough to start a free radical chain reaction. However, it can interact with reactive free radicals, thereby reducing the free radicals numbers and inhibiting overall free radical reaction chain. Consequently, the gas yield was reduced while DOC content was increased due to the addition of alanine. The influence of proteins on hydrothermal gasification of carbohydrates is shown in Fig. 7. As biomass may contain both proteins and salts, increased gas yield resulting from salts catalysis can compensate the negative effect of proteins on gas yield to some extent [60].

3.4. Alcohols

Alcohols can be formed under hydrothermal conditions [24]. Methanol, glycerol, and ethylene glycol are three typical model compounds used in SCWG for hydrogen production. Methanol is the simplest compound for reforming in SCW. Methanol reforming was conducted at 27.6 MPa and 700 °C to produce H₂, CH₄, CO, and CO₂, which was catalyzed by the reactor wall [76]. Results suggested that methanation reactions were favored under high pressures, long residence time, and low steam/carbon ratio. Ni–Cu in the tubular reactor can minimize the CH₄ production. The main reactions in methanol reforming, including methanol

Table 2
Summary of chemical reactions involved in this article.

Reaction type	Stoichiometric reaction equation	Reaction number
Simplified overall reaction of SCWG	$\text{CH}_x\text{O}_y + (2-y)\text{H}_2\text{O} \rightarrow \text{CO}_2 + (2-y+x/2)\text{H}_2$	(1)
Steam reforming	$\text{CH}_x\text{O}_y + (1-y)\text{H}_2\text{O} \rightarrow \text{CO} + (1-y+x/2)\text{H}_2$	(2)
Water–gas shift reaction	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, $\Delta H_{298\text{K}} = -41.0 \text{ kJ/mol}$	(3)
Methanation of CO	$\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$, $\Delta H_{298\text{K}} = -206.2 \text{ kJ/mol}$	(4)
Methanation of CO ₂	$\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$, $\Delta H_{298\text{K}} = -165.0 \text{ kJ/mol}$	(5)
Decarboxylation	$\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2$	(6)
Dehydration	$\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O}$	(7)
Formation pathways of OH radicals	$\text{H}_2\text{O} + \text{M} \rightleftharpoons \text{OH} + \text{H} + \text{M}$, (M represents a collision partner)	(8)
	$\text{H}_2\text{O} + \text{H} \rightleftharpoons \text{OH} + \text{H}_2$	(9)
	$\text{H}_2\text{O} + \text{O} \rightleftharpoons \text{OH} + \text{OH}$	(10)
	$\text{OH} + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{O}_2$	(11)
	$\text{OH} + \text{HR} \rightleftharpoons \text{H}_2\text{O} + \text{R}$	(12)
	$\text{H}_2\text{O} + \text{HO}_2 \rightleftharpoons \text{OH} + \text{H}_2\text{O}_2$	(13)
Hydrogen formation route	$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} \rightarrow 6\text{CO}_2 + 12\text{H}_2$, Endothermic, $\Delta n = +13$	(14)
Methane formation route	$\text{C}_6\text{H}_{12}\text{O}_6 \rightarrow 3\text{CO}_2 + 3\text{CH}_4$, Slightly exothermic, $\Delta n = +5$	(15)
Overall reaction for SCWG of glucose	$\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} \rightleftharpoons 6\text{CO}_2 + 12\text{H}_2$, $\Delta H_{298\text{K}} = +360.86 \text{ kJ/mol}$	(16)
Methanol decomposition	$\text{CH}_3\text{OH} \rightleftharpoons \text{CO} + 2\text{H}_2$, $\Delta H_{298\text{K}} = +91.7 \text{ kJ/mol}$	(17)
Catalytic mechanism of K ₂ CO ₃ in SCWG	$\text{K}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{KHCO}_3 + \text{KOH}$	(18)
	$\text{KOH} + \text{CO} \rightarrow \text{HCOOK}$	(19)
	$\text{HCOOK} + \text{H}_2\text{O} \rightarrow \text{KHCO}_3 + \text{H}_2$	(20)
	$2\text{KHCO}_3 \rightarrow \text{H}_2\text{O} + \text{K}_2\text{CO}_3 + \text{CO}_2$	(21)
	$\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{HCOOH} \rightleftharpoons \text{H}_2 + \text{CO}_2$	(22)
Overall SCWG of cellulose with Ca(OH) ₂	$\text{CH}_x\text{O}_y + (1-y)\text{H}_2\text{O} + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + (2-y+x/2)\text{H}_2$	(23)
Enhanced steam–methane reforming	$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2 + \text{CO}$, $\Delta H_{298\text{K}} = 206.2 \text{ kJ/mol}$	(24)
Cu deactivation reaction by sulfur	$2\text{Cu} + \text{H}_2\text{S} \rightleftharpoons \text{Cu}_2\text{S} + \text{H}_2$, $\Delta H_{298\text{K}} = -59.4 \text{ kJ/mol}$	(25)

decomposition, water–gas shift reaction, and methanation [77] can be found in Table 2.

Due to the complicated functional groups and ring-structure in 5-HMF formed during hydrothermal gasification of glucose, glycerol becomes a simpler and better model compound. Besides, glycerol could partly represent glycerolipids [78]. Bühler et al. [79] investigated hydrothermal decomposition of glycerol in near- and supercritical water under 349–475 °C and 25, 35, or 45 MPa within 32–165 s using a tubular reactor. The main products were methanol, acetaldehyde, propionaldehyde, acrolein, allyl alcohol, ethanol, formaldehyde, CO, CO₂, and H₂. Qadariah et al. [80] recently reported the degradation of glycerol in a batch reactor under 200–400 °C and 30 MPa with a reaction time of 20–60 min. They claimed that acetaldehyde and allyl alcohol were only formed in subcritical water and SCW, respectively. Acrolein can be formed in both conditions. The highest glycerol conversion rate of 99.92% can be obtained. SCWG of glycerol for hydrogen production has also been carried out [78,81,82]. Compared with other sewage sludge model compounds (i.e. glucose, glycine, lauric acid, and humic acid), glycerol showed the highest carbon conversion in Raney nickel catalyzed SCWG [78]. In the presence of Ru/Al₂O₃, H₂ with low CH₄ and CO was produced at 700–800 °C in a tubular fixed-bed flow reactor within 5 s [81]. Complete conversion of glycerol was obtained under 510 and 550 °C with 1 wt% Ru/ZrO₂, but the complete gasification was not possible as acetic acid and acetaldehyde were difficult to be gasified. The carbon deposits from polymerization of high concentration of acetic acid also reduced hydrogen yield [82].

de Vlieger et al. [83] carried out catalytic reforming of ethylene glycol in SCW under 450 °C and 25 MPa using Ir, Pt, and Ni based mono- and bi-metallic catalysts. High Pt loading exhibited highest hydrogen yield while low Pt loading had an adverse effect on hydrogen selectivity and catalyst stability. The primary liquid by-products were methanol, ethanol, and acetic acid [50]. The Pt–Ni/Al₂O₃ was suggested to improve hydrogen yield by inhibiting CH₄ production and acetic acid. Since acetic acid was associated with the hydroxylation of the Al₂O₃ support, suppressed acetic acid could prolong the lifetime of catalysts.

3.5. Lipids

SCWG of oleic acid (C₁₈H₃₄O₂, a model compound for lipids) was conducted at 28 MPa with three temperature levels of 400, 450, and 500 °C [1]. At 400 °C, long chain fatty acids were formed via hydrolysis of oleic acid but saturated acids were resistant to hydrolysis below 300 °C. As temperature increased, hydrogen yield increased with the primary liquid products of aromatic and cyclo-compounds formed at 450 °C, but heptanoic and hexanoic acids, cresol, and ketones formed at 500 °C. It was speculated that hydrogen was produced from dehydrogenation processes and water–gas shift. The Diels–Alder cyclization was responsible for cyclo-compounds formation.

3.6. Effect of feedstock nature

Performance of SCWG is closely associated with type and concentration of feedstocks. A wide variety of biomasses, such as lignocellulosic woody biomass, chicken manure, food wastes, fermentation residues, sewage sludge, and algae have been successfully gasified in SCW [17]. Conventional lignocellulosic biomass consists of cellulose (38–50%), hemicellulose (25–32%), and lignin (15–25%) [84]. Cellulose and hemicellulose are carbohydrates whereas lignin is a complex compound with high molecular weight and composed of three highly cross-linked phenylpropane units of *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol via ether bonds (C–O–C) and C–C bonds [85,86]. On the other

hand, sewage sludge is typically consisted of proteins (40%), lipids (10–25%), carbohydrates (14%), lignin and ash (30–50%) [2], and less heavy metals, pathogens or other microbiological pollutants, and POPs. The sewage sludge varies from different sources and processes. For example, the digested sludge contains considerable but recalcitrant organic matter, including lignin compounds [87]. In comparison to sludge from WWTPs, Zhang et al. [87] reported that the secondary pulp/paper-mill sludge (SSP) produced high hydrogen yield. Apart from the higher contents of volatile matter and alkali salts therein, a better performance of hydrogen production may also be associated with the high pH value of SSP. Even though some constituents contained in real biomass are similar with pure model compounds, SCWG process may be significantly different due to interactions of different constituents. The existence of sulfur and other minerals can even lead to catalyst deactivation in catalytic hydrothermal gasification process [17].

As the concentration of feedstock increases, carbonaceous deposits from undesired side reactions can lead to a decrease of the hydrogen selectivity in the reforming of glucose [53]. According to studies of supercritical water partial oxidative gasification under 650 °C and 25 MPa [88], the fraction of H₂ decreased from 29.3 to 10.14% and the yield of hydrogen decreased from 8.939 to 1.933 mol/kg when concentrations of glucose was increased from 10 to 24%. This may be associated with limited reaction rates of hydrolysis and water–gas shift. Muangrat et al. [89] reported that yields of CO, CO₂, CH₄, and C₂–C₄ increased, whereas the hydrogen yield reduced as the feed concentration increased in partial oxidative gasification of food-based biomass. Under this context, it is imperative to gain more insights into relationships between the gas evolution profile and chemical composition of biomass material.

4. Catalytic hydrothermal gasification

It is of particular interest to integrate catalytic process into thermochemical biomass conversion process to improve the yield and quality of gas or liquid fuels [90]. Introduction of catalysts (either homogeneous or heterogeneous) in hydrothermal gasification could achieve good gasification performance under mild temperatures and pressures, lowering the operating cost and equipment investment. Therefore, latest applications of homogeneous and heterogeneous catalysts in hydrothermal gasification are discussed herein.

4.1. Homogeneous catalysts

The catalytic effect of alkali salts in improving the water–gas shift has been widely reported in literature. Muangrat et al. [89] conducted partial oxidative gasification of food-based biomass, including glucose, molasses, and rice bran, with the aid of H₂O₂ in alkali hydrothermal conditions. The tar/oil and char were not found because of the presence of alkali. It was addressed that NaOH had a positive effect on the hydrogen yield via water–gas shift. By examining cellulose decomposition under catalytic hydrothermal conditions at temperatures from 200 to 350 °C, Minowa et al. [21] verified the important role of alkali materials (i.e. sodium carbonate) in inhibiting char formation from oil. The addition of alkali salts also increased the H₂ and CO₂ yields but decreased the CO yield [40,91]. The catalytic effect of the alkali salts can be explained by the improvement of water–gas shift reaction resulting from the formation of formate salt in the presence of alkali salts [92]. Sinağ et al. [92] proposed the catalytic mechanism of K₂CO₃ in SCWG in reactions (18)–(22). Besides, alkali salts can accelerate C–C bonds splitting to increase

Table 3

Summary of catalytic hydrothermal gasification of model compounds and real biomass for hydrogen rich gas production using various heterogeneous catalysts.

Feedstock	Experimental condition	Reactor type	Catalyst	Experimental results and remarks	Reference
Cellulose, sawdust	500 °C, 27 MPa, 20 min	Stainless steel 316L 140 mL high-pressure autoclave	Ru/C, Pd/C, CeO ₂ particles, nano-CeO ₂ , nano-(CeZr) _x O ₂	The catalytic activity was Ru/C > Pd/C > nano-(CeZr) _x O ₂ > nano-CeO ₂ > CeO ₂ particles. By adding sodium carboxymethylcellulose, the 10 wt% cellulose or sawdust can be completely gasified.	[101]
Lignin	400 °C, 37.1 MPa, water density 0.5 g/cm ³	Stainless steel 316 tube bomb reactor	Ru/TiO ₂ , Ru/γ-Al ₂ O ₃ , Ru/C	The initial catalytic activity was high and in the order of Ru/TiO ₂ > Ru/γ-Al ₂ O ₃ > Ru/C; Ru/C and Ru/γ-Al ₂ O ₃ gradually lost high lignin gasification activities which can be ascribed to decreased surface area and dissolution of ruthenium active sites resulting from phase change of γ-Al ₂ O ₃ .	[102]
Methanol	700 °C, 27.6 MPa, < 1 min	Stainless steel 316 tubular reactor	Copper nanoparticles continuously generated from cupric acetate in feedstock	In-situ generated copper nanoparticles were highly active in SCWG of methanol in 15 s. The reactor was suitable for sulfur-containing feedstock as sulfur can be removed out by forming Cu ₂ S in the continuous flow reactor.	[77]
Glycerol	700–800 °C, < 5 s	Tubular fixed-bed flow reactor	Ru/Al ₂ O ₃	Ruthenium exhibited high activity for C–C bond cleavage for H ₂ rich gas formation; H ₂ decreased whereas CH ₄ increased as the glycerol concentration was increased to 40%. Short residence time reduced CH ₄ production.	[81]
Polyethylene glycol	390 °C, 24 MPa, 60–300 s	Continuous reactor, Inconel 625	Ni/ZrO ₂	Catalytic activity was 5% Co/15% Ni/ZrO ₂ > 5% W/15% Ni/ZrO ₂ > 5% Ni/ZrO ₂ > 15% Co/ZrO ₂ > ZrO ₂ > 15% W/ZrO ₂ > NiO/ZrO ₂ ; ZrO ₂ can suppress methanation reaction and Ni/ZrO ₂ inhibited toxic intermediates production.	[103]
Glucose, cellulose, sewage sludge	450 °C, 47.1 MPa, 60 min	Batch reactor, Inconel 625, 10.8 cm ³	RuO ₂	RuO ₂ achieved complete SCWG of cellulose into H ₂ , CH ₄ , and CO ₂ ; RuO ₂ can be deactivated by sulfur compounds	[104]
Cellulose and lignin	SCWG at 400–525 °C, 10 and 15 min, water density 0.05–0.18 g/cm ³	Capillary quartz reactor	Nickel, iron, copper, zinc, zirconium wires, ruthenium powder, and Raney nickel slurry	All the tested metal (except copper) produced H ₂ from SCW in the absence of biomass; catalysts surface area/biomass weight ratio was critical in increasing gas yields; 40–50% energy content in cellulose and lignin could be recovered in gas when using nickel wires; Ruthenium powder presented low activity.	[94]
Glucose	600 °C, 24 MPa, WHSV 3.0 and 6.0 h ^{−1}	Continuous-flow tubular reactor	Ni, Ru, Cu and Co supported on γ-Al ₂ O ₃ , ZrO ₂ , and Activated carbon (AC)	Ru and Ni supported on γ-Al ₂ O ₃ showed highest activity and H ₂ selectivity among catalysts investigated; Ni based catalytic activity on support materials for H ₂ production was γ-Al ₂ O ₃ > ZrO ₂ > AC; Ru and Mg effectively promoted Ni/γ-Al ₂ O ₃ by suppressing coke and tar formation.	[98]
Oleic acid	400–500 °C, 28 MPa, 30 min	Batch reactor, Hastelloy C-276, 600 mL	Ru/Al ₂ O ₃ , Ru/AC, Pt/AC, Pd/AC, Ni/SiO ₂ –Al ₂ O ₃	Catalytic activity for H ₂ production was pelletized Ru/Al ₂ O ₃ > powder Ni/SiO ₂ –Al ₂ O ₃ > powder Pt/AC > granular Ru/AC > powder Pd/AC; Ni/SiO ₂ –Al ₂ O ₃ and Ru/Al ₂ O ₃ achieved 96% and 86% COD reduction efficiency, respectively; ruthenium favored the methane formation at the cost of consuming H ₂ ; significant deactivation of Ru/Al ₂ O ₃ and Ru/C were observed.	[1]
Glucose	380 °C, 23 MPa, 15 min	Batch reactor, stainless steel, 50 mL	Nickel supported on α-Al ₂ O ₃ , carbon nanotubes (CNTs), MgO, SiO ₂ , Y ₂ O ₃ , hydrotalcite, yttria-stabilized zirconia (YSZ), TiO ₂ , γ-Al ₂ O ₃ , zeolites, molecular sieves, CeO ₂ , ZrO ₂	At 5% Ni loading, carbon conversion followed the order: α-Al ₂ O ₃ , CNT, and MgO > SiO ₂ , Y ₂ O ₃ , hydrotalcite, YSZ, and TiO ₂ ; different γ-Al ₂ O ₃ supports showed a wide range of catalytic activities and may not be practically used in SCWG. Increased Ni loading of Ni/α-Al ₂ O ₃ resulted in an increasing H ₂ selectivity; K, Ca, Cs promoted while Sn decreased the catalytic activity of Ni/α-Al ₂ O ₃ .	[24]
Water solubles from biomass pyrolysis	350 °C, 20 MPa, LHSV 45 h ^{−1}	Continuous fixed-bed reactor	Ni/C, Ni–Pt/C	Impregnation of Pt into Ni/C improved carbon conversion to higher than 99.9%.	[105]
Ethylene glycol	450 °C, 25 MPa, WHSV 5.9 and 17.8 h ^{−1}	Continuous reactor	Pt–Ni/Al ₂ O ₃ , Pt/Al ₂ O ₃	Pt–Ni bimetallic catalyst enhanced H ₂ yield with two-fold higher activity than monometallic Pt catalyst. Addition of Ni prevented sintering of Pt particles.	[83]
				Acetic acid deactivated Pt/Al ₂ O ₃ and Pt–Ni/Al ₂ O ₃ through the hydroxylation of Al ₂ O ₃ support and re-deposition of Al(OH) _x on catalytic Pt sites	[50]
Ethylene glycol, Acetic acid	450 °C, 25 MPa, 6 h, 2 mL/min	Continuous reactor	Pt/CNT	Pt/CNT was a stable and effective catalyst for SCWG of ethylene glycol and acetic acid.	[106]
Glucose	400 °C, 24.5 MPa	140 mL stainless steel autoclave	Ni/CeO ₂ /Al ₂ O ₃	Addition of Ni/CeO ₂ /Al ₂ O ₃ increased H ₂ yield and selectivity dramatically due to the role of CeO ₂ in inhibiting carbon formation by increasing Ni dispersion and reacting with deposited carbon.	[96]

hydrogen production [38]. Recently, Trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) was proved to be an economical natural mineral catalyst as effective as K_2CO_3 , and it increased the hydrogen yield by seven-fold in SCWG of acorn under 600 °C and 35 MPa [91].

Apart from aforementioned studies, Onwudili and Williams [46] also investigated the role of sodium hydroxide in promoting hydrogen production from hydrothermal gasification of glucose and other biomass materials from 200 °C and 2 MPa to 450 °C and 34 MPa at a constant water content. Two different processes for hydrogen formation were proposed: (1) hydrogen gas produced via water gas shift using the CO released from decarbonylation of hydroxylated carbonyl compounds; and (2) hydrogen gas released from the reaction of sodium carboxylate with water. The removal of CO_2 as sodium carbonate or bicarbonate improved the formation of hydrogen gas.

In practice, the trade-off between yield and purity of hydrogen still exists. He and Chen [93] proposed a one-step sorption-enhanced steam reforming procedure to improve hydrogen yield and selectivity using dolomite as CO_2 acceptor. Guo et al. [25] found hydrogen yield in SCWG of cellulose in the presence of $\text{Ca}(\text{OH})_2$ was almost twice of that without catalyst and very low concentrations of CO_2 and CO could be achieved because of CO_2 capture by $\text{Ca}(\text{OH})_2$. The overall SCWG of cellulose with $\text{Ca}(\text{OH})_2$ is described in reaction (23).

Though alkali catalysts are effective to promote hydrogen yield, issues pertaining to corrosion, plugging, and fouling may be induced by them [16]. In order to achieve a high hydrogen yield with minimized detrimental effects, the optimal alkali content in feedstock is essential.

4.2. Heterogeneous catalysts

Compared to homogeneous catalysts, heterogeneous catalysts present higher hydrogen selectivity, CGE, as well as easier recyclability [16]. In the past decades, catalytic hydrothermal gasification (CHG) has been extensively explored. Table 3 listed studies on CHG of model compounds and real biomass for hydrogen rich gas production using various heterogeneous catalysts in recent years.

4.2.1. Nickel catalysts

Due to relatively low cost of nickel catalysts, nickel based catalysts have been extensively applied in petrochemical industries. Cortright et al. [51] developed APR to convert carbohydrates into H_2 and gaseous alkanes at a low temperature and medium pressure. Resende and Savage [94] quantified the catalytic effect of metals,

including nickel, iron, copper, zinc, and zirconium wires, ruthenium powder, and Raney nickel slurry, on SCWG of cellulose and lignin in quartz reactors. A measurable increase of gas yield can be achieved when using a catalyst surface area to biomass weight ratio higher than 15 mm^2/mg . Nickel and copper with a loading ratio of 5.0 wt% was proved to obtain higher gas yield. Moreover, nickel with a loading ratio of 1.0 wt% gave the highest hydrogen yield while copper exhibited no background hydrogen formation in the absence of biomass feedstock under SCWG conditions. The presence of metals had little influence on CH_4 yield. The oxidation of metals is commonly found under hydrothermal conditions. Only nickel and copper can remain reduced in the metallic form among base metals and nickel can be active in numerous formulations whereas the effective lifetimes rely on the support materials [15]. On the contrary, nickel oxide hardly exhibits any catalytic activity.

Raney nickel catalysts are prepared by leaching out aluminum from Ni–Al alloy with concentrated sodium hydroxide to form Ni catalyst with a spongy structure [17]. Fresh Raney nickel possesses a specific surface area ranging from 50 to 100 m^2/g , which is far higher than that of metal powder and wire catalysts, i.e. $\ll 1 \text{ m}^2/\text{g}$. In addition, Raney nickel exhibited beneficial hydrogen yield in near-critical water gasification [95]. It has been noted that hydrogen selectivity may be enhanced by increasing the metal loading due to the high sensitivity of methanation reaction to metal dispersion. Due to preparation methods, a considerable amount of hydrogen may be stored in Raney nickel, which can be one order of magnitude higher than that chemisorbed on catalyst surface. Under hydrothermal conditions, the release of stored hydrogen as well as that from partial oxidation of nickel by water may cause misleading results of anomalously higher hydrogen in final gas yield [17]. Therefore, the examination of background hydrogen formation from catalysts is essential before conducting CHG.

Alkali or alkaline earth metals, such as Na, K, Ca, Mg, and Ru, are proved effective to enhance metal dispersion and retard Ni sintering, thus they were previously used as promoters to reduce coke formation in CH_4 reforming with CO_2 . Azadi et al. [24] summarized the addition of alkali metal (i.e. K, Na, and Cs) enhanced the hydrogen selectivity and carbon conversion of Ni/ $\alpha\text{-Al}_2\text{O}_3$ while Sn decreased the catalytic activity. Lu et al. [96] studied the effect of Ce loading in Ni-based catalyst (i.e. Ni/ $\text{CeO}_2/\text{Al}_2\text{O}_3$) on catalytic activity and carbon deposition in SCWG of glucose at 400 °C and 24.5 MPa. Because of the lattice oxygen on the surface of CeO_2 , carbon deposition on the catalyst was inhibited and thus catalytic activity was enhanced by adding CeO_2 . On the other hand, the surface area of catalysts decreased

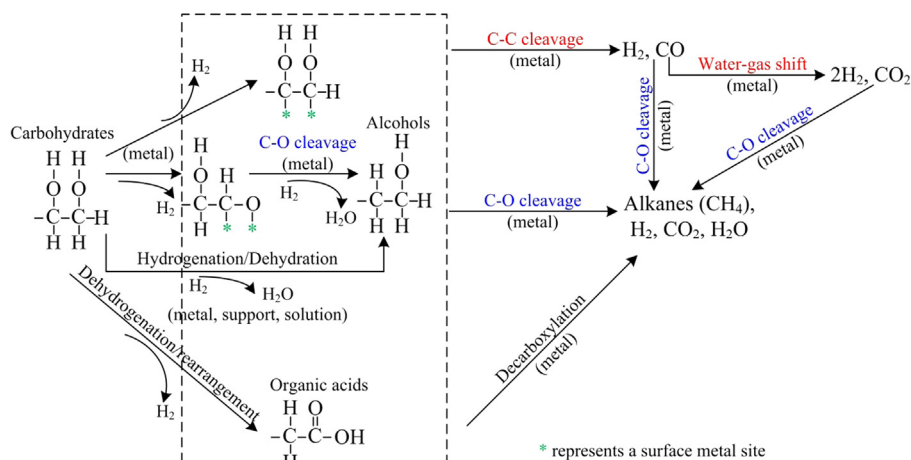


Fig. 10. Reaction pathways for catalytic hydrothermal gasification of carbohydrates for hydrogen production (adapted from [24,51]).

^d Calculated as grams TOC per gram liquid sewage sludge sample, assuming the density of liquid sample was 1 g/mL.

crystalline nature and open structure, which can enhance the mass transfer and decrease the possibility of coke blockage.

4.2.5. Deactivation of catalysts

Char formation has been observed in decomposition of cellulose, glucose, and sugars under sub- and supercritical water. Promoters are often incorporated into nickel based catalysts to prevent carbon deposition. It is the encapsulating carbon rather than the filamentous carbon that should be responsible for the deactivation of catalysts [111,112]. Because of nucleic growth of filaments, metal particles can be lifted off the support and thus remain the accessibility to reactants. Compared with nickel, Ni–Cu alloys are more effective for formation of filamentous carbons, in which Cu can inhibit the formation of encapsulating carbon and enhance the stability of Raney-Ni in the methane decomposition at 600 °C [111]. Kim et al. [113] identified that alkyl substituted C5 ring hydrocarbons were responsible for the formation of polycyclic aromatic hydrocarbon which could result in coke formation during decomposition of methylcyclohexane in SCW. During methanol reforming at 700 °C and 27.6 MPa [77], Cu can be significantly deactivated by sulfur through the reaction (25).

5. Sewage sludge treatment using SCW

Because of the high organic matter and water content in sewage sludge, SCWG is an emerging technology suitable for sewage sludge treatment and energy recovery. SCWO is an oxidation process closely related to SCWG, which functions as “wet incineration” in hydrothermal conditions by using strong oxidants (e.g. H_2O_2 , O_2 , and KMnO_4) to completely destruct organic matter in SCW. SCWO was originally developed more than 30 years ago at Massachusetts Institute of Technology for NASA [7]. Various applications of SCWO have been implemented in defense industry. For instance, the U.S. Navy designed a shipboard SCWO plant to destroy the Navy excess hazardous materials, while the U.S. Army and U.S. Air Force used SCWO for destruction of obsolete nerve gas, biological weapons and other munitions [7,114].

5.1. Feasibility of SCWG of sewage sludge for hydrogen rich fuel gas

Xu et al. [115] demonstrated the first SCWO pilot plant in China with a treatment capacity of 125 kg/h for sewage sludge harmless treatment. The SCWO showed particular advantages over incineration of sewage sludge in terms of lower operating cost and harmless treatment products. It was pointed out that more by-products income could further reduce the operating cost. Therefore, optimization of hydrogen yield from SCWG of sewage sludge is of great interest to facilitate the commercialization of this technology.

Meanwhile, Xu et al. [116] investigated the potential feasibility of direct SCWG of sewage sludge with moisture contents ranging from 76.2 to 94.4 wt%. However, as the moisture content decreased, total gas yield decreased with a substantial reduction of CO_2 yield and slight reduction of H_2 and CH_4 . It was proved that carbonization process was accelerated in lower moisture content and thus the obvious reduction of CO_2 yield can be ascribed to the carbon transformation into coke therein. Guo et al. [25] claimed that higher reaction temperature was required for high concentration feedstocks to achieve complete gasification in SCWG of sludge.

Table 4 summarizes the SCWG of sewage sludge with and without catalysts in terms of gaseous composition, carbon/hydrogen gasification rate and hydrogen yield. Most of the studies were focused on the activated sludge with solid content less than 5 wt%, which exhibited hydrogen yield 15.49 mol/kg dry sludge [117] but may not be economical for practical treatment of the huge volume

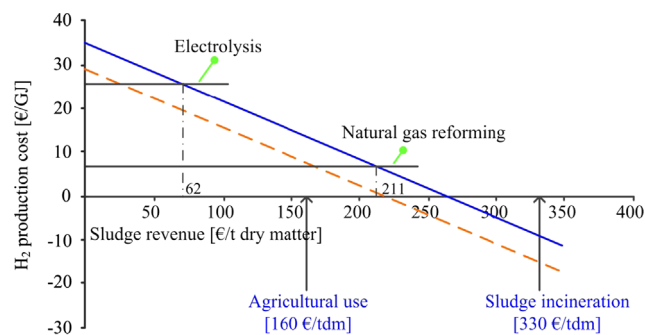


Fig. 11. Hydrogen production costs vs. sewage sludge revenues, base case (solid line) and learning case (dotted line) (adapted from [122]).

of sewage sludge. The hydrogen production from SCWG is only of significance in industrial application when a solid concentration of sewage sludge higher than 15% is applied. However, for those SCWG of dewatered sludge or digested sludge with solid loading higher than 8 wt%, the hydrogen yield is limited with lower CGE. In fact, Zhang et al. [99] proposed a combined hydrothermal liquefaction of simulated biomass waste and catalytic SCWG of aqueous products from hydrothermal liquefaction to harvest heavy oil and hydrogen rich gas simultaneously. Recently, a pre-liquefaction process of sewage sludge and wood sawdust in subcritical water was found to enhance H_2 and CH_4 yield [118,119]. Since the majority of organic compounds in sewage sludge can be hydrolyzed and dissolved in near-critical water, a two-stage hydrothermal gasification process could be feasible. In the first stage, near-critical water gasification process can hydrolyze the majority of organic compounds in sewage sludge into water soluble products and generate a part of hydrogen. In the subsequent stage, the CHG of aqueous products is employed to generate more hydrogen, where catalysts can be easily recovered via solid–liquid separation thereafter.

5.2. Technical and economic evaluation

SCWG is regarded as an emerging technology for sewage sludge treatment as well as hydrogen production. Gasafi et al. [120] determined the cost of hydrogen production and revenues from sewage sludge disposal using the total annual revenue requirement method. As it can be seen in Fig. 11, when sewage sludge revenue exceeds 211€/t dry matter, SCWG is competitive for hydrogen production from natural gas reforming (6.82 €/GJ) while SCWG is comparable to electrolysis (26.82 €/GJ) if the revenue can exceed 62 €/t dry matter. Though SCWG is suitable for hydrogen production of biomass, Calzavara et al. [121] claimed that technological improvements (i.e. reactor engineering and catalysts) are indispensable for industrial scale-up. Importantly, combustion of methane should be taken into consideration. Due to the great amount of non-reactant water, overall energy efficiencies are 15% and 50% based on LHVs of $\text{H}_2 + \text{CO}$ and $\text{H}_2 + \text{CO} + \text{CH}_4$, respectively, under the classical recovery efficiency of 80%.

5.3. Perspectives on technical issues

This review article highlights that hydrothermal gasification is a promising technology for hydrogen rich fuel gas production from sewage sludge or other biomass wastes. Nevertheless, three key problems concerning corrosion, plugging and high operating cost still exist, making some commercial scale SCWO of sewage sludge plants inactive [115]. Due to harsh hydrothermal conditions, issues pertaining to hydrothermal gasification must be addressed to make this technology economically and practically feasible in

industrial applications. The challenges associated with corrosion, high operating cost, reactor plugging and catalyst deactivation are discussed as follows.

At elevated temperatures and pressures, water can be highly acidic, basic, oxidizing, or reducing in specific hydrothermal conditions. Generally, stainless steel and nickel based alloys are used reactor materials in hydrothermal decomposition. During SCWG of glucose [35], Ni, Cr, and Mo, which are the constituents of reactor wall, can be detected in the solid phase as a result of corrosion, indicating corrosion of the reactor wall. In addition, heteroatoms in sewage sludge can form corrosive acids in hydrothermal environment. A comprehensive review pertaining to corrosion issues under hydrothermal conditions can be found elsewhere [128]. Both equipment-based and process-based approaches could be applied for corrosion control. Though Hastelloy reactor is highly corrosion-resistant, the high construction cost may be uneconomical. Acceptable corrosion control can be achieved via combination of proper corrosion-resistant materials, chemical control, process control, and mechanical design [129].

The severe hydrothermal conditions may hinder wider applications to some extent. Moreover, to achieve complete destruction of biomass with maximum gasification rate, feedstock concentrations less than 5% are generally used, which could further increase the operating cost. A series of pre-treatment, chemical conditioning, and CHG should be employed in future investigations to run the hydrothermal gasification under economically reasonable feedstock concentrations and milder temperatures/pressures.

Inorganic alkali salts can be used as homogeneous catalysts in CHG. On the contrary, due to decreased solubility of inorganic compounds, the precipitated salts may cause plugging in the continuous reactor. Besides, high temperatures and pressures can result in metal sintering and phase change of support materials, which shorten the lifetime of catalysts. Sulfur poisoning and coke deposition can also deactivate catalysts. To mitigate these three key issues, a two-stage hydrothermal gasification concept could be a promising strategy to handle sewage sludge with high solid loading by incorporating catalytic process in the second stage.

6. Conclusions

Hydrothermal gasification is an attractive technology to produce hydrogen rich fuel gas from sewage sludge. This article has summarized the effect of various reaction conditions and intermediates on gas composition and hydrogen yield during sub- and supercritical water gasification. As sewage sludge is a complicated mixture of organic compounds, studies of hydrogen production from hydrothermal conversion of biomass model compounds have provided fundamental understanding to maximize hydrogen gasification efficiency and hydrogen yield. Besides, both homogeneous and heterogeneous catalysts are applied to enhance hydrogen yield and purity. Though alkali salts are economical, corrosion and fouling issues induced by them are concerns. Noble metals are efficient heterogeneous catalysts to improve yield and selectivity of hydrogen, while appropriate promoters and hydrothermally stable support materials are desired. According to previous studies on near critical and supercritical water gasification of sewage sludge, it is technically feasible to recovery H_2 and CH_4 rich gas. However, issues regarding corrosion, plugging and high operating cost are challenging in commercial applications. To mitigate these drawbacks, a two-stage hydrothermal gasification concept is proposed, which may achieve optimal hydrogen production under mild temperature and pressure by incorporating a catalytic process.

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